

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) IMPROVED REACTION METHOD

(71) We, THE UPJOHN COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 301 Henrietta Street, Kalamazoo, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

### Background of Invention

This invention relates to a method for commingling a plurality of liquids, and more particularly relates to a high velocity blending method for commingling a plurality of liquid reactants in a manner to minimize the creation of by-products.

It is well known to blend two or more high velocity streams of liquid reactants to produce a third component, and it is also well known to employ such blending techniques in those instances where at least one of the components is also undesirably sensitive to the resulting material sought to be produced. For example, it is well known to selective blend a high velocity stream of liquid amine into a high velocity stream of liquid phosgene to produce a liquid isocyanate. The amine is also reactive with the isocyanate sought to be produced, however, and thus any amine molecules which escape phosgenation tend to react with the isocyanate to produce urea-containing substances.

These by-products are extremely undesirable for many reasons. In the case of the urea-containing substances, for example, the by-products not only reduce the quality and value of the isocyanate, they constitute a solid or semi-solid material which tends to progressively clog the ports in the contacting structure to the extent that liquid flow is gradually reduced and ultimately completely blocked. When this occurs, the process must be entirely shut down and the contactor must be disassembled and cleaned, before production can be resumed at a normal rate.

It is a practical impossibility to achieve total elimination of all by-products created during the operation of blending processes of this character, since this would require that the blending process operate with perfect efficiency. The impossibility of such a goal will be more apparent if it is realized that, in the production of isocyanate, perfect efficiency would require that each and every molecule of amine injected into the process be instantly surrounded or contacted by phosgene before engaging any isocyanate molecules.

Production shut-downs are obviously undesirable, however, and thus many attempts have been made to develop improved blending techniques, reducing the proportion of by-products generated. In the phosgenation of amine to produce isocyanate, for example, it is conventional to blend a proportionally small flow rate of amine into a proportionally heavy rate of phosgene, in an attempt to overwhelm the amine with phosgene, since the phosgene is non-reactive with the isocyanate and since it may be reclaimed without adverse affect on the isocyanate sought to be produced. Other blending devices have been developed, such as that depicted in U.S. Patent No. 3,321,283, which employ mechanical agitation and churning to intermix the phosgene and amine at the point of interaction. Although apparatus of this character will provide better blending than that obtained by the basic intermixture of the two streams, such apparatus is complex and expensive. Furthermore, such apparatus is quite difficult to clean after clogging has developed.

Accordingly, these disadvantages of the prior art have been substantially eliminated or reduced by the present invention, and novel mixing methods and apparatus are provided herein which are suitable for commingling phosgene and the like with a liquid amine and the like, whereby the production of unwanted substances such as urea-containing by-products is substantially reduced or eliminated to a practical degree.

According to the invention there is provided

a method of continuously chemically reacting a first liquid reactant with a second liquid reactant to form a liquid product and to provide for reduced secondary reaction between the second reactant and the reaction product comprising the steps of conducting a stream of first reactant along a first annular flow path, conducting a stream of second reactant along a second annular flow path which flares outwardly in a downstream direction to join said first flow path at an acute angle, and combining and reacting said reactants downstream of the junction of said first and second paths, the liquids after being combined at the junction being caused to flow together downstream.

As will hereinafter be disclosed in detail, a preferred form of apparatus for carrying out the method of the present invention is embodied in reaction contactor apparatus having no moving parts, but providing for the establishment of a high velocity stream of amine which joins a high velocity stream of phosgene preferably at an angle which may be substantially ninety degrees or less, whereby isocyanate is carried away from the point of junction to substantially reduce the opportunity of amine - isocyanate interactions to occur. Further, the structure is preferably adapted to establish restricted flow paths for both the phosgene and the amine immediately prior to junction of the flow paths, to prevent backflow of isocyanate into either of the flow paths upstream of the point of junction of the paths due to the development of eddy currents or churning in the streams.

Another disadvantage of some devices of the prior art is that the amine stream is directed along a path downstream of the junction point which is located parallel to and adjacent one or more surfaces in the structure. Although such an arrangement has the advantage of reducing churning and other turbulence and thus reduced backflow of isocyanate, such a structure tends to cause the amine to flow as a sheath along the surface and into the isocyanate without interacting with the phosgene. In the structures illustrated herein, however, this disadvantage has been eliminated by establishing that the amine stream is injected into the phosgene stream in a direction non-parallel to all structural surfaces at and downstream of the point of junction of the phosgene and amine flow paths.

In the drawing:

Figure 1 contains a pictorial representation, partly in cross section, of an exemplary form of apparatus for producing isocyanate by the phosgenation of a suitable amine according to the method of the present invention.

Figure 2 contains a pictorial view of the amine input end section of the apparatus illustrated in Figure 1.

Figure 3 contains a cross-sectional representation of another portion of the apparatus illustrated in Figures 1 and 2.

Referring now to Figure 1, there may be seen an exemplary form of apparatus for producing isocyanate or the like, and basically composed of a hollow tee-shaped housing 2 containing a hollow sleeve member 11 disposed in the cross-bar portion of the housing 2, and further containing a flow adjustment device disposed within the sleeve member 11. As illustrated in Figure 1, phosgene enters through a phosgene input port 3 in the end of the leg portion of the housing 2 and flows about the exterior surface of the sleeve member 11. The sleeve member 11 is disposed so as to block one end of the cross-bar portion of the housing 2 and is provided with a plurality of amine input ports 10 at one end whereby the amine may flow through the sleeve member 11, and out the other end to commingle with the phosgene, to produce isocyanate which exists through the isocyanate output port 22 in the other end of the cross-bar portion of the tee-shaped housing 2.

The housing 2 may be provided with conventional flanges 4, 7 and 21, for interconnection with other liquid conducting structures (suggested but not depicted), may be provided with suitable gasket surfaces 5, 9 and 33, whereby a fluid-tight seal may be obtained with the use of a flat gasket 13 or other suitable sealing means. In addition, the sleeve member 11 may have a flange-like end portion 34 for engaging gasket 13 to seal the housing 2 adjacent flange 7, and may also have an upset shoulder 31 and a spacing flange or rib 20 for supporting the sleeve member 11 in a centralized manner within the cross-bar portion of the housing 2. A flared bell-like velocity collar 29, which is preferably fashioned of a very hard substance such as tungsten carbide, may be welded or otherwise fixedly attached to the opposite end of the sleeve member 11 as illustrated, for the purposes which will hereinafter be explained.

As may also be seen in Figure 1, the aforementioned flow adjustment device may be composed of a cylindrical positioning rod 12 threadedly inserted through the center of the flange-like end 34 of the sleeve member 11, and may have a plurality of spacing ribs 19 located along its length for centrally supporting it within the sleeve member 11. Since the positioning rod 12 may be selectively positioned longitudinally within the sleeve member 11, it is preferably provided with a threaded end section 17 and a suitable retaining nuts 16 which, together with a suitable shim or washer 18, function to secure the shaft member 12 within the sleeve member 11. At the other end of the shaft member 12, there may be provided a suitable conically-formed fairing member 27, which is

preferably formed of a hard substance such as tungsten carbide, and which may be threadedly connected to the shaft member 12 by means of threads 28 or any other suitable means. The fairing member 27 may be seen to be selectively spaced close to but from the inside surface of the velocity collar 29 to establish a narrow gap 26, which may be conical or disc-like, and which forms amine flowing along the positioning rod 12 into a correspondingly shaped jet or stream.

The velocity collar 29 hereinbefore described may be seen to have an outside diameter larger than that of the sleeve member 11, and thus is established a restricted gap 25 which is smaller than the cross section of the phosgene flow annulus 23 established between the exterior of the sleeve member 11 and the inside surface of the cross-bar portion of the housing 2. Thus, it will be seen that the amine stream is accelerated immediately before entering the phosgene stream at a preselected angle of generally ninety degrees or less, and that the phosgene stream is similarly accelerated and formed into a cylindrical jet or stream by flowing through the restricted gap 25 located immediately before such junction. Accordingly, it will be apparent that the reaction area of the amine and phosgene will be at and immediately downstream of the point or region of junction of the cylindrical phosgene stream by the jet of amine, and that the resulting isocyanate is carried downstream to the output port 22 adjacent flange 21.

In most of the prior art mixing structures and techniques now in general commercial use, the amine stream is merely injected in the manner of a jet into a bath or flow of phosgene. Although the turbulence created by the injection tends to facilitate dispersion of the injected amine, it will be apparent that this technique unavoidably establishes a constant area of high amine concentration in the phosgene which is conducted downstream to commingle with the isocyanate. As stated in the aforementioned Patent No. 3,321,283, where the isocyanate or other intended reaction has a half-life on the order of 0.005 to 0.1 second, it is extremely important to reduce the dispersal time of the amine or other primary reactant, especially where competing reactions lower the yield as hereinbefore explained.

Accordingly, it is proposed in Patent No. 3,321,283, to provide mechanical mixing means for churning the commingling amine and phosgene at a velocity whereby nearly complete dispersal of the amine may be accomplished within the period less than the half-life of the reaction sought to be achieved, and whereby the primary reactants (amine and phosgene) are completely mixed before half of the heat of reaction is evolved. There can be no question but what the technique

described in Patent No. 3,321,283 is capable of substantially accomplishing this result. However, it should also be realized that no technique can achieve phosgenation of the entire amine input, no matter how efficacious the technique may be, and thus an amount of by-product will always be produced and will accumulate in the mixing apparatus. Thus, even apparatus such as that described in Patent No. 3,321,283, will eventually become clogged, and this in itself is especially disadvantageous since such equipment is far more difficult than conventional mixing apparatus to disassemble and clean. Moreover, such apparatus is not only expensive and complex to purchase and maintain, but it is expensive to power, and thus a simpler reaction contactor having no rotating or moving parts is generally employed especially where there are competing reactions producing unwanted solid or semi-solid substances.

Other prior art structures and techniques have been proposed from time-to-time, such as may be seen in Patent No. 3,154,103, and which involve the use of reaction contactors which simply blend the amine and phosgene streams without the use of moving or rotating mechanical whippers. Most of these contactors operate to create turbulence in the streams for blending purposes, and while the turbulence is beneficial, the structures and techniques so employed or suggested have also tended to create eddy currents causing backflow of isocyanate into the mixing regions, or they create a flow of amine along one or more surfaces whereby a flow of amine is created which tends to slide downstream in the phosgene without effective intermixing with the phosgene.

Referring now to Figure 1, it will be seen that the tendency to establish either an isocyanate backflow, or an area of high amine concentration, has been substantially reduced or eliminated in the present invention by the high velocity junction of the phosgene flow path by the amine flow path at an angle preferably ninety degrees or less, whereby the two streams tend to drive the isocyanate away from the point of junction and into the expanding reaction area formed downstream by the inside surface of the tungsten carbide insert 30 and the tapering surface of the fairing member 27. The particular angle will generally depend on the reaction sought to be achieved, since the speed of the reaction between the amine and phosgene determines the location of the initial molecules of isocyanate. Accordingly, the angle is functionally related to the reaction rate of the process intended to be maintained.

Another feature, however, is the restriction provided in the two flow paths by the structures illustrated herein. As hereinbefore stated, these restrictions provide acceleration of the streams immediately upstream of and adja-

cent to the point of junction, to provide substantially instantaneous dispersion of amine into the larger phosgene stream without the necessity of rotating or moving mechanical agitating devices. Furthermore, such acceleration assists to a substantial extent in preventing isocyanate backflow.

In structures of the type illustrated herein, it is conventional to develop fluid velocities of forty to sixty feet per second, or greater, and this tends to have an eroding effect on the portions of the structure adjacent these streams. Accordingly, it is preferable that the fairing member 27, the velocity collar 29, and the insert 30 all be formed of a hard erosion-resistant material such as tungsten carbide or the like.

As hereinbefore stated, the reaction of amine with isocyanate tends to proceed quite rapidly. In many of the structures of the prior art, the amine stream tends to be directed substantially parallel to one or more adjacent surfaces of the structure past the point of junction of the phosgene stream, in order to minimize erosion of the surface. In such an arrangement, however, a flowing film or layer of amine tends to be established on the surface, which layer also tends to flow into the isocyanate to create the unwanted urea-containing by-products.

This disadvantage of the prior art is avoided with the structures illustrated in Figure 1, wherein the amine stream flowing in gap 26 is angularly positioned relative to all surfaces downstream of the junction of the amine and phosgene streams. In other words, the amine stream is angularly positioned both as to the insert 30 and the tapering downstream portion of the conical fairing member 27.

Referring again in Figure 1, it may be seen that the flange-like end section 34 of the sleeve member 11 is preferably adapted to provide a fluid-tight connection with any upstream amine-conducting structures which may be connected thereto. Accordingly, the flange-like end section 34 may also be provided with a suitable gasket surface 15 on its upstream side, as illustrated in Figure 1.

Referring now to Figure 2, there may be seen an end view of that portion of the housing 2 which includes flange 7, including a pictorial representation of bolt holes 8 therein, as gasket surface 9 and gasket 13. As may be seen, the threaded end section 17 of shaft 12 is centrally located in the flanged-like end portion 34 of the sleeve member 11, and is secured therein by retaining nuts 16 and the washer or shim 18. In addition, a plurality of amine input ports 10 may be seen to be arranged circularly and concentrically about the flanged end portion 34 of the sleeve member 11, in an equally spaced-apart manner. As may be seen in Figure 1, these amine input ports are all directed to the interior of the sleeve member 11, to ensure that amine

flow is substantially equal about the entire surface of the shaft member 12.

Referring now to Figure 3, there may be seen a cross-sectional representation of the structure illustrated in Figure 1, showing the cylindrical configuration of the cross-bar portion of the housing 2, and showing the cylindrical sleeve member 11 centrally disposed within the housing 2 to provide a phosgene flow annulus 23. As may also be seen in Figure 3, the cylindrical shaft member 12 is centrally disposed within the sleeve member 11 by means of the equally spaced-apart spacing ribs 19, to provide the amine flow annulus 24.

Although the structures illustrated herein have been found to be particularly advantageous in the phosgenation of amines to produce isocyanates, it should be understood that the structures and methods are not limited in usefulness to the production of isocyanates. Instead, any process involving high velocity liquid blending to achieve rapid reaction can employ the structures and techniques described and illustrated herein, especially if such processes employ a reactant which interacts with the end product sought to be obtained as hereinbefore explained.

#### WHAT WE CLAIM IS:—

1. A method of continuously chemically reacting a first liquid reactant with a second liquid reactant to form a liquid product and to provide for reduced secondary reaction between the second reactant and the reaction product comprising the steps of conducting a stream of first reactant along a first annular flow path, conducting a stream of second reactant along a second annular flow path which flares outwardly in a downstream direction to join said first flow path at an acute angle, and combining and reacting said reactants downstream of the junction of said first and second paths, the liquids after being combined at the junction being caused to flow together downstream.

2. A method as claimed in claim 1 including the step of accelerating said first reactant flow along said first path immediately prior to the past the junction of said paths.

3. A method as claimed in claim 1 or claim 2 including the step of accelerating said reactant flow along said second path immediately prior to the past the junction of said paths.

4. A method as claimed in any preceding claim wherein said second flow path joins said first path at an angle functionally related to the reaction rate.

5. A method as claimed in any preceding claim wherein the second flow path is substantially frusto-conical.

6. A method as claimed in any preceding claim including the step of controlling the velocity flow of the second reactant with respect to that of the first reactant.

7. A method as claimed in any preceding claim of continuously reacting phosgene, as the first reactant, with an amine, as the second reactant, to produce an isocyanate.
- 5 8. A method of reacting liquid phosgene with a liquid amine reactant to produce an isocyanate with reduced secondary reaction of the amine and the isocyanate, substantially as described herein.
- 10 9. A method as claimed in any preceding claim carried out in apparatus substantially as described herein with reference to the accompanying drawings.
10. An isocyanate produced by the method of reaction claimed in any of claims 1 to 9. 15

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COMPLETE SPECIFICATION

1 SHEET

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